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Rheology of starch–milk–sugar systems: effect of heating temperature

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Abstract

This study aims to investigate the effect of heating temperature on the rheological behavior of starch–milk–sugar (SMS) pastes. Different concentrations of corn and wheat starch were heated in liquid skim milk containing 8 wt% sugar at 60, 75, 85 and 95 °C. The sugars used are glucose, sucrose and fructose. The pastes heated at 60 and 75 °C show the same low value of viscosity. As the heating temperature increased to 95 °C, a great increase in the apparent viscosity of the paste was observed. This means that the degree of gelatinization of starch heated at 60 and 75 °C was insignificant. On the other hand, the pastes exhibited a time-independent behavior at low heating temperature (60 and 75 °C) and changed to a thixotropic behavior with increasing the heating temperature. One exception was the 2 wt% wheat–milk–glucose paste, which shows an antithixotropic behavior. The Herschel–Bulkley model was used to fit the flow curves of SMS pastes. The yield stress and the consistency coefficient increased with increasing the heating temperature and starch concentration, reflecting the increase in paste viscosity.

Keywords: Wheat starch; Corn starch; Sugar; Milk; Heating temperature; Rheology

1. Introduction

Starches are extensively used in a variety of food products such as ice cream, chocolate, milk-based sweets, jellies, sauces, custards and desserts. In these products, the method of preparation such as water content, temperature and the presence of other organic/inorganic materials is an important factor that determines the rheological behavior of starch dispersions (STDs) (Master & Steeneken, 1997; Willet, Jasberg, & Swanson, 1995).

In Jordan, starches are also used in milk-based desserts such as 'SAHLAB'. There are no standard procedures for the manufacture of these products. Therefore studying the changes in the flow behavior, which might occur during the process, will help in establishing methods of producing an acceptable product with consistent quality.

Starch is a natural polymer, the monomer of which is glucose. It exists in two forms: straight and branched. Amylose is a straight chain, water insoluble polymer of glucose, while the amylopectin is a branched chain, water-imbibing polymer of glucose (Bailey & Ollis, 1986). All starches are made up of these two polysaccharides and the ratio varies with the starch botanical source. On heating in excess water, the amylopectin structure melts, and the granules swell in a process known as gelatinization. The degree of gelatinization structure of starch depends upon the cooking process and the type of starch utilized. Roos (1992) have defined gelatinization as collapse (disruption) of molecular orders within the starch granule, manifested by irreversible changes such as granule swelling, native crystallite melting and starch solubilization. During cooling, retrogradation occurs when solubilized starch polymers and remaining granules reassociate in an ordered structure.

The gelatinization temperature range is usually 5–10 °C. The initial gelatinization temperature of wheat starch in water was found to be in the range of 55–66 °C and for corn starch in water was found to be in the range of 65–76 °C (Roos, 1992).

The effect of cooking temperature on the rheological properties of heated starch in water has received much attention in the literature. Ellis, Ring, and Whittam (1989) investigated the viscous behavior of aqueous suspensions of gelatinized wheat and maize starches. The swelling and deformability of gelatinized wheat starch granules showed a strong dependence on the heating rate employed to gelatinize the starch.

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Corn starch was subjected to thermo-mechanical processing of varying degrees of severity. These treatments ranged from gentle dissolution to autoclaving at temperatures up to180 °C, to jet cocking. The treatments had major effects on viscosities of the STDs. The dispersions of jet-cooked corn starch exhibited non-Newtonian flow behavior (Dintzis & Bagley, 1995).

Chamberlain, Rao, and Cohe (1999) showed that cross-linked waxy maize (CWM) dispersions (2.6 wt%) in water, heated in the range 60–120 °C, exhibit shear thinning behavior. On the other hand, dispersions heated for 15 min at 60 °C showed slight shear thickening. Power law model was used to characterize the flow behavior of STD.

Rao and Tattiyakul (1999) studied the influence of granule size on the rheological behavior of 2.6% tapioca STDs. Compared to corn and cowpea starches, heated tapioca starch granules had a higher initial maximum diameter, which was less dependent on the heating temperature. Shear thickening flow behavior was observed in STDs heated at 61 °C for 1, 5 and 15 min, and shear thinning behavior in all other dispersions.

Ahmad and Williams (1999) investigated the effect of sugars on the thermal and rheological properties of aqueous sago starch. Sugars were found to increase the gelatinization temperature in the following order (water alone) < ribose < fructose < glucose < maltose < sucrose. The swelling factors in the presence of sugar were higher compared to (water alone) for sugar concentrations below 25% but were lower at sugar concentration greater than 25%.

The aim of this study was to investigate the effect of heating temperature on the rheological behavior of heated starch–milk–sugar (SMS) systems. Two kinds of starch were used, namely; wheat and corn. Whilst corn starch is commonly used by the food industry as a thickening agent, wheat starch is becoming increasingly available. Three different types of sugar were also used in this study; glucose, fructose and sucrose.

2. Materials and methods

2.1. Materials

Wheat starch was obtained from Chemlab Company, England. Corn starch was obtained from Suppilco chemicals (pharnma grade). Glucose and fructose anhydrous powder (MW = 180.16; 99% extra pure) were obtained from S.D. Fine Chemicals, Ltd. Local grade sucrose was provided from the united farmer and industry company, Ltd., Thailand. Pasteurized fresh liquid milk (fat content = 0.2%) obtained from Al-Asria Dairy Company, Jordan, was used in this study. A mother buffer phosphate solution (0.01 M, pH of 7) was prepared to control the pH.

2.2. Viscometer

The steady rheological properties of starch were measured using a concentric cylinder viscometer (Haake VT 500, MV3—system) which has an inner cylinder rotating in a stationary outer cylinder. Details of the viscometer system are provided in Abu-Jdayil (2002). The viscometer was thermostatically controlled with a water circulator (Haake D8).

The apparent viscosity (η) of starch pastes as a function of shear rate ($\dot{\gamma}$) was measured. The measurements were carried out with increasing (forward measurements) and decreasing (backward measurements) shear rates. The shear rate was varied between 2.20 and 219.8 s^{-1}. To predict the flow curves (shear stress, τ, versus shear rate) the following equation was used:

$$\tau = \eta\dot{\gamma} \quad (1)$$

2.3. Heating method

Weighed samples of starch (2–6 wt%) and sugar (8 wt%) were blended with cold liquid milk in a jacketed vessel. The pH was measured before heating and regulated to 7 by adding phosphate buffer. STD was heated with hot water transferred by a pump from a water bath to the jacketed vessel. Agitation during heating was achieved using a magnetic stirrer. Continuous stirring was maintained until the desired temperature of 60, 75, 85 or 95 °C was reached. The samples were kept at the desired temperature for a period of time of 30 min. Then samples were allowed to cool and stored over night at room temperature before conducting the rheological tests. All rheological tests were performed at 25 °C.

3. Results and discussion

3.1. Corn starch–milk–sugar (CMS) paste

The CMS pastes prepared at 60 and 75 °C have nearly the same rheological behavior. These samples have nearly the same apparent viscosity, which decreases with increasing the shear rate; characterizing a shear-thinning behavior, see Fig. 1. It was observed that the corn starch granules at 60 and 75 °C still suspended in milk and slightly swelled which explains the relatively low viscosity of CMS paste using different starch concentrations. In addition, the forward and backward measurements of the apparent viscosity did not show hysterises loops under shearing cycles, i.e. the forward and backward measurements superimpose each other, indicating that the starch gelatinization at these temperatures is insignificant. Hysterises indicates some type of dependency of viscosity on time of shearing.

As the heating temperature increased to 95 °C the apparent viscosity of the paste increased and some type of

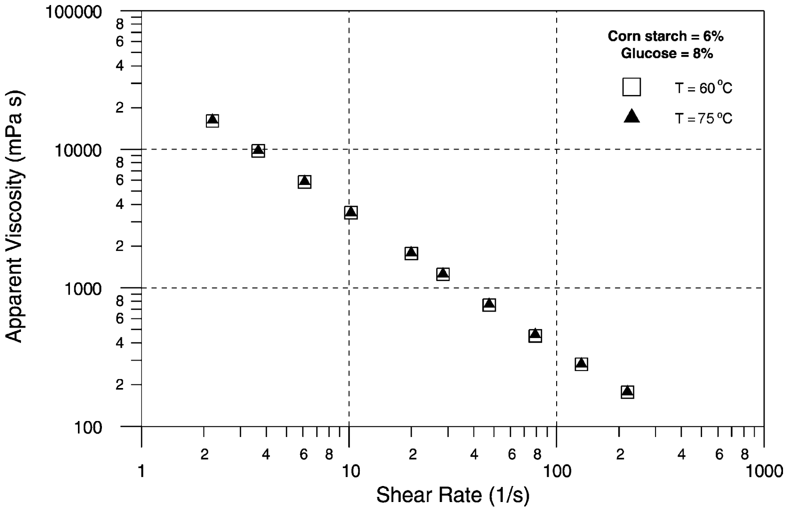

Fig. 1. Apparent viscosity of CMS paste prepared at 60 and 75 °C.

the hysteresis loops is present indicating a large percentage of granules being gelatinized. The pastes prepared at high temperatures exhibited a thixotropic behavior; where the viscosity decreases with time of shearing, see for example Fig. 2. Increasing the heated temperature softened the granules and the stresses imposed on them were large enough for deformation and flow, and in turn resulted in the increase in the thixotropic behavior (Chamberlain et al., 1999). This thixotropic behavior was found to be more pronounced (wider hysterises loops) with increasing the heating temperature and the starch concentration, compare Figs. 2 and 3. The heating temperature changes the structure of CMS paste from a dispersion fluid type at 75 °C to a medium gel structure at 85 °C and to a strong gel product at 95 °C. This has been assessed by visual observations.

It is clear that the gelatinization temperature of CMS paste is greater than that of corn starch–water system, which was found to be in the range of 65–76 °C (Roos, 1992). This increase in the gelatinization temperature can be attributed to the presence of sugar (Ahmad & Williams, 1999). Perry and Donald (2002) found that the addition of sugars and other polyols to starch–water systems elevates the starch gelatinization temperature. They explained this phenomenon that the reduced level of solvent plasticization, resulting from the addition of non-aqueous solutes to the pure water system, which results in the elevation of the gelatinization temperature. A reduced level of solvent plasticization of the amorphous growth ring regions requires that a greater level of thermal energy be input before the starch granule can swell and begin to gelatinize.

According to the change of viscosity with the heating temperature, the viscosity can be considered as a qualitative property to define the degree of gelatinization. For starch

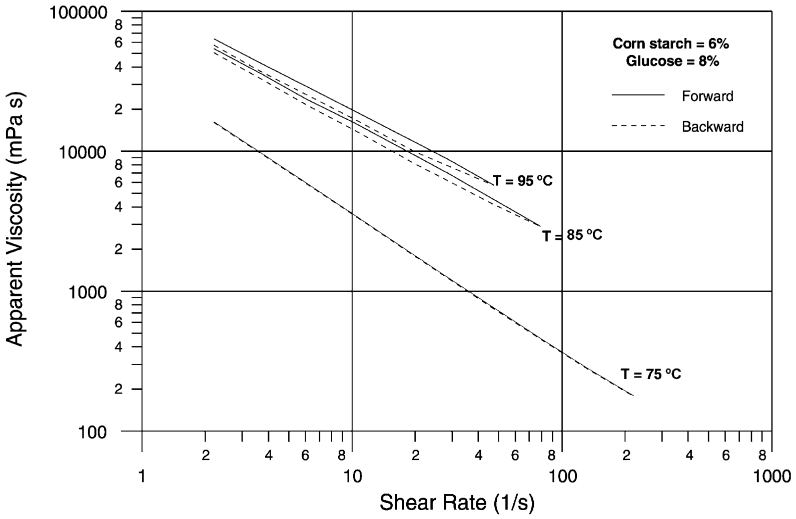

Fig. 2. Hysterises loops of 6 wt% CMS paste heated at different temperatures.

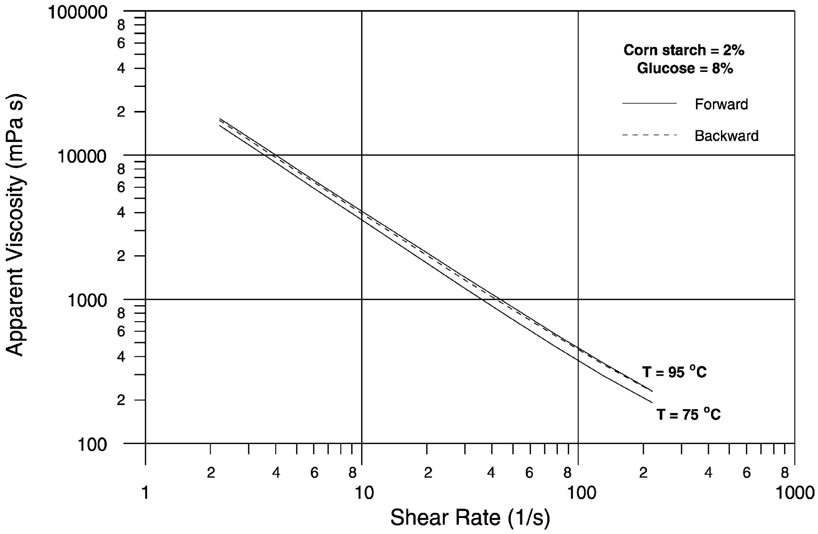

Fig. 3. Hysterises loops of 2 wt% CMS paste heated at different temperatures.

concentration of 6 wt%, the apparent viscosity of corn starch–milk–glucose paste at $\dot{\gamma} = 2.20\ s^{-1}$ has increased by 233% when the heating temperature is increased from 75 to 85 °C and show a small increase (about 17%) when the heating temperature is increased from 85 to 95 °C. This leads to a conclusion that the CMS paste might be completely gelatinized above 85 °C. The same behavior was also found with other types of sugars (sucrose and fructose). The effect of heating temperature on the gelatinization of the corn starch is in consistent with the findings of Rao, Okechukwu, Da Silva, and Oliveira (1997). They observed that granules swelled to about 3–4 times their initial size during isothermal heating of corn starch. They showed also that the initial average diameter (D_0) of corn starch granules was increased from 13.5 to 32.8 μm after heating for 30 min at 80 °C. In another study, Ellis et al. (1989) found the gelatinization temperature for corn starch in water to be 65 °C and by raising the heating temperature to 90 °C, the swelling ratio (gram swollen starch per gram dry starch) was raised from 3.5 to 12.

The flow curves of the CMS paste prepared at different temperatures and using 8 wt% sugar were fitted by the Herschel–Bulkley (H–B) model:

$$\tau = \tau_0 + m\dot{\gamma}^n \tag{2}$$

where n is the flow behavior index, m is the consistency coefficient, and τ_0 is the yield stress. The degree of fit of individual experimental data curves to the H–B model was found to be very good ($R^2 \geq 0.97$), see for example Fig. 4 that shows the flow curves of CMS paste using sucrose. The regressed parameters of H–B model at different heating temperatures using different types of sugars are shown in Table 1. The results, generally, confirm the above findings. More investigation of the yield stress (τ_0) values in Table 1

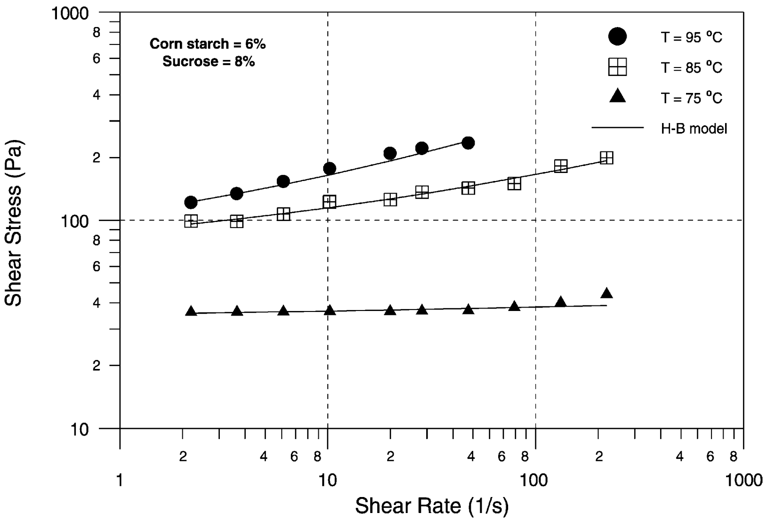

Fig. 4. Flow curves of 6 wt% CMS paste heated at different temperatures and fitted to H–B model.

Table 1
Parameters of H–B model for CMS paste prepared at different temperatures using 8 wt% sugar

Sugar type	Starch conc. (wt%)	Heating temperature (°C)								
		τ_0 (Pa)			m (Pa s^n)			n		
		95	85	75	95	85	75	95	85	75
Glucose	6	85	75	33	44.1	25.4	4.3	0.37	0.30	0.16
	4	45	44	32	6.6	6.0	2.3	0.34	0.30	0.16
	2	35	34	32	3.2	2.8	4.3	0.27	0.25	0.15
Sucrose	6	65	63	31	43.0	25.4		0.36	0.30	0.11
	4	43	33	30	6.2	4.3	2.3	0.34	0.19	0.11
	2	33	32	29	2.9	2.8	2.0	0.26	0.19	0.10
Fructose	6	60	59	30	43.0	25.4	4.1	0.35	0.30	0.11
	4	40	32	29	6.1	4.2	2.2	0.34	0.19	0.11
	2	33	32	28	2.8	2.8	1.95	0.25	0.18	0.10

shows that the effect of starch concentration of the rheology of CMS paste becomes more pronounced with increasing the heating temperature. In addition, the m values (measure of viscosity) demonstrate that the gap in the viscosity between the CMS pastes prepared at 75 and 85 °C can be reduced as the starch concentration decreases keeping the sugar concentration constant. On the other hand, the flow behavior index (n) values show that the CMS paste deviates form the shear thinning behavior to the plastic behavior (n approaches unity with a yield stress), as both the starch concentration and heating temperature increase.

3.2. Wheat starch–milk–sugar (WMS) paste

The WMS pastes prepared at 60 and 75 °C have nearly the same viscosity. Contrary to the CMS pastes, the WMS samples show a very narrow clockwise hysterises loops under shearing cycles indicating a small percentage of granules were gelatinized as shown in Fig. 5 for the fructose paste. The clockwise hysterises indicates some type of dependency of viscosity on time that could be identified as a thixotropic behavior. This leads to the conclusion that the degree of gelatinization of WMS past at 60 and 75 °C is greater than that of CMS paste, and this can be attributed to the fact that the initial gelatinization temperature of wheat starch in water is less than that of corn starch. It has been shown (Perry & Donald, 2002) that the elevation of gelatinization temperature (or gelatinization temperature range) is qualitatively the same whatever the starch cultivar or added sugar. Variations in starch cultivar only result in differences in the absolute magnitude of the temperature elevation associated with each solution.

Starch granules are insoluble in cold milk, but they swell as heated and crystallites become disordered. As the heating temperature increased from 75 to 95 °C the apparent viscosity increased and the hysteresis loops became wider indicating

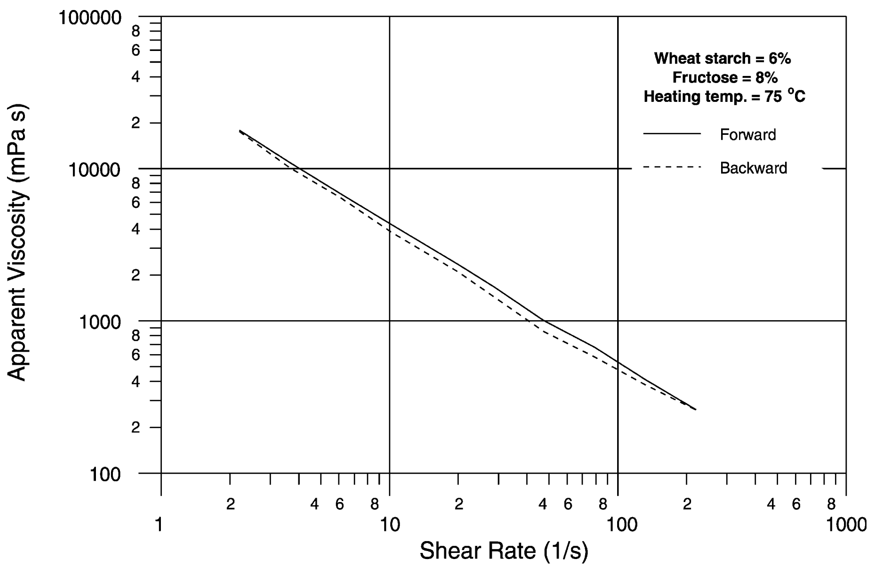

Fig. 5. Hysterises loops of 6 wt% WMS paste heated at 75 °C.

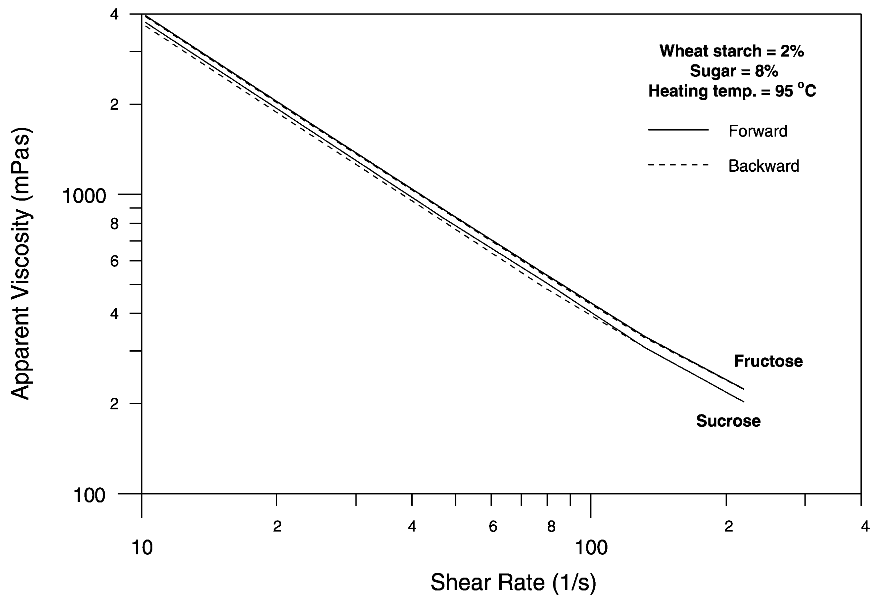

Fig. 6. Hysterises loops of 2 wt% WMS paste heated at 95 °C using sucrose and fructose.

a large percentage of granules being gelatinized. Ellis et al. (1989) provided in their study for wheat starch that as the temperature increased from 65 to 90 °C the swelling ratio (gram swollen starch per gram dry starch) was increased from 6.4 to 14.8. Increasing in swelling ratio means an increase in the apparent viscosity.

The prepared WMS pastes using fructose and sucrose show a thixotropic behavior for all starch concentrations used, see for example Fig. 6. On the other hand, the WMS paste using glucose shows a thixotropic behavior at high starch concentration (4 and 6 wt%) and an antithixotropic behavior at low starch concentration (2 wt%). As shown in Fig. 7, the antithixotropic behavior of paste in presence of glucose is clear at different heating temperatures. Previous investigation attributed antithixotropic behavior in retorted CWM STDs without sugar to shear-induced granula cluster formation (Chamberlain et al., 1999). As the dispersions were sheared, starch granules rearranged to form clusters that, in turn, resulted in an increase in apparent viscosity. In our case, it seems that at high starch concentrations (4 and 6 wt%), shear-induced cluster were not formed. In the same respect, Acquarone and Rao (2003) found that the 5 wt% CWM STDs heated at 85 and 110 °C in 0–30 wt% sucrose solution exhibited antithixotropic behavior, while those

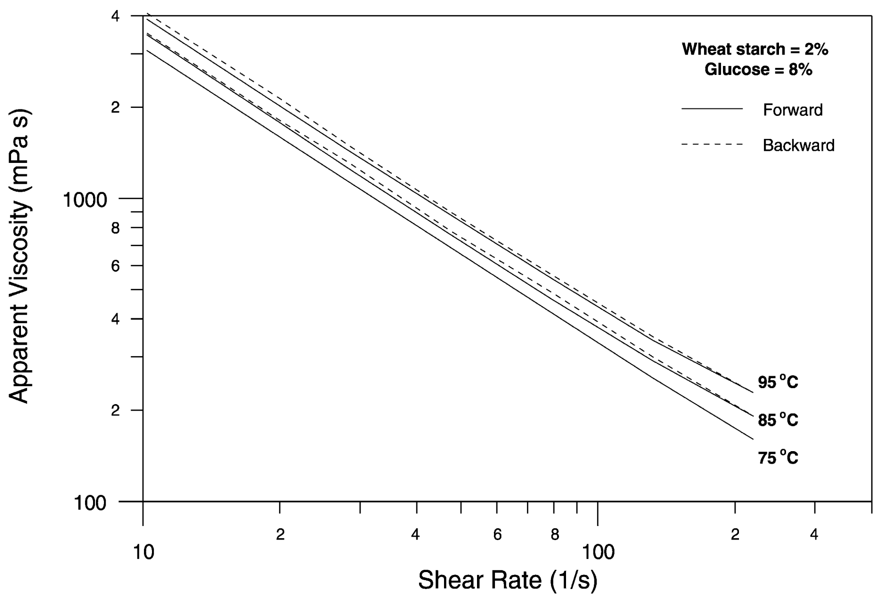

Fig. 7. Hysterises loops of 2 wt% WMS paste heated at 95 °C using glucose.

Table 2
Parameters of H–B model for WMS paste prepared at different temperatures using 8 wt% sugar

Sugar type	Starch conc. (wt%)	Heating temperature (°C)								
		τ_0 (Pa)			m (Pa s^n)			n		
		95	85	75	95	85	75	95	85	75
Glucose	6	65	55	30	49.3	49.6	5.3	0.35	0.32	0.20
	4	42	40	29	11.7	11.5	5.3	0.25	0.25	0.12
	2	34	32	28	3.1	2.3	2.2	0.21	0.21	0.10
Sucrose	6	70	60	31	52.7	48.7	6.6	0.37	0.32	0.25
	4	42	41	29	13.2	12.2	6.1	0.28	0.25	0.20
	2	35	32	29	3.1	2.9	4.3	0.25	0.25	0.24
Fructose	6	71	62	32	52.7	49.0	6.7	0.39	0.33	0.25
	4	53	49	6.7	14.9	12.3	6.3	0.30	0.27	0.24
	2	43	42	30	3.2	3.0	4.5	0.26	0.25	0.23

heated in 40–60 wt% sucrose solution exhibited thixotropic behavior. Further investigations experiments on the time-dependent behavior of SMS paste may clarify the role of system parameters (e.g. starch concentration, sugar type and concentration, etc.) in the rheology of such paste.

From the values of the H–B model parameters, reported in Table 2, it can be seen that the consistency coefficient and the yield stress of WMS pastes increased with increasing the starch concentration and heating temperature. In addition, Table 2 shows that increasing the heating temperature from 85 to 95 °C lead to small increase in m and τ_0 values of WMS paste. On the other hand, there is a significant difference between the H–B parameters of pastes prepared at 75 and 85 °C. This leads to a conclusion that the WMS paste can be completely gelatinized above 85 °C. Table 2 shows also that the gap in H–B parameters between the pastes prepared at 75 °C and that prepared at 85 °C can be increased as the starch concentration increases.

In Fig. 8 we compare the apparent viscosity of CMS paste with that of WMS paste prepared at different temperatures. At heating temperatures of 85 and 95 °C, where it is expected that both pastes are completely gelatinized, the CMS pastes show higher viscosity than the WMS paste. One reason could be that the granula of glatinized corn starch is more anisometric than that of galtinized wheat starch (Ellis et al., 1989). The rotation of anisometric particles in a shear field leads to a greater perturbation of that field, and hence greater increase in viscosity than that produced by spheres of the same volume.

At low heating temperature, 75 °C, the viscosity of WMS paste is greater than that of CMS paste. It is likely that

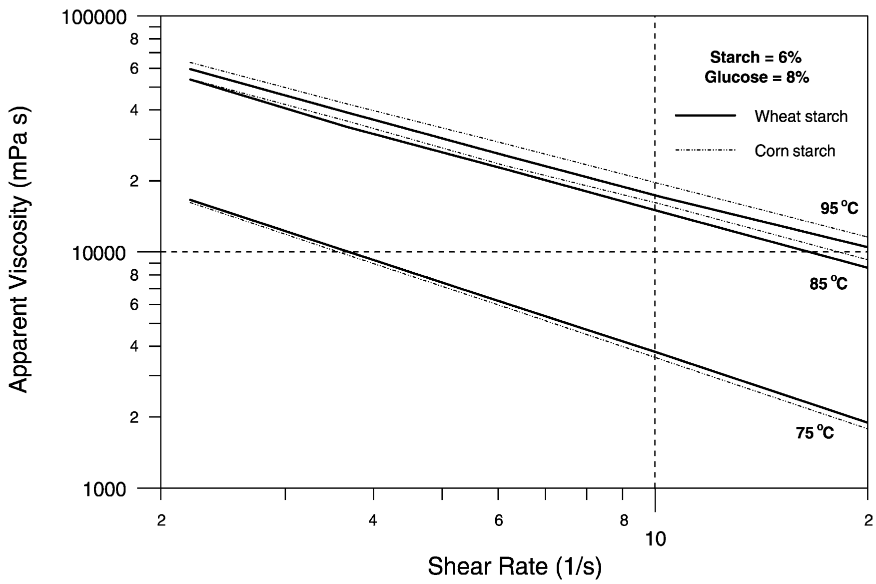

Fig. 8. Coparison between the CMS and WMS pastes heated at different temperatures.

the degree of gelatinization of WMS paste at 75 °C is greater than that of CMS paste.

4. Conclusions

The addition of sugars to starch–milk systems elevated the starch gelatinization temperature compared to the gelatinization of starch–water system. The degree of gelatinization of WMS paste heated at 75 °C was insignificant but greater than that of corn starch based paste. This was assessed from the low value of the paste viscosity. A considerable increase in the paste viscosity was observed when the heated temperature was increased to 95 °C. The greatest relative increase in the paste viscosity was observed when the heated temperature raised from 75 to 85 °C, which means that most of the starch gelatinized at 85 °C.

The results confirm also that starches from different botanical sources are different in their pasting behavior. The CMS paste exhibited a time-dependent rheological behavior when prepared at 75 °C, and a thixotropic behavior when prepared at 85 or 95 °C. The thixotropic behavior was more clear at high starch concentration. On the other hand, the WMS paste exhibited a thixotropic behavior at all heated temperatures in the presence of fructose and sucrose. The WMS paste prepared with glucose show a thixotropic behavior at 4 and 6 wt% starch concentration, and an antithixotropic behavior at 2 wt% stach concentration. The latter behavior was attributed to shear-induced granula claster formation.

Finally, it should be stated that the CMS paste exhibited higher viscosity that WMS paste except those prepared at 75 °C, wher the viscosity of WMS paste was greater. It is likely that the degree of gelatinization of WMS paste at 75 °C was greater than that of CMS paste.

Acknowledgements

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